EXAM 4

November 22, 2017

IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.

Give units for all quantities!

YOUR NAME SOLUTIONS

Some data: $R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ 1 atm = 101325 Pa

$dU = dq + dw$ $dS = dq_{rev}/T$ $\gamma = C_p/C_V$ $C_p - C_V = nR$

$dw = -p_{ex}\, dV$ Heat engine $\varepsilon = (T_h - T_c)/T_h$ adiabat: $pV^{\gamma} = \text{const}$

$H = U + pV$ $G = H - TS$ $A = U - TS$

$k = A \exp(-E_a/(RT))$ mean K.E. = $1.5\ k_B T$

$d \ln K/d(1/T) = -\Delta H/R$ $\Delta_r G = \Delta G^o + RT \ln Q$

(1) *30 points*

Consider the reaction A → B which has the rate law $v = k[A]^3$. Initially $[A] = a_0$. Prove that $[A]^{-2} = 2kt + 1/a_0^2$ and use this result to determine the half-life of A. *Show work.* Give an example of appropriate units for k.

$$v = k[A]^3 = -\frac{d[A]}{dt} \quad \therefore \quad \frac{d[A]}{[A]^3} = -k\,dt$$

$$\therefore \int \frac{d[A]}{[A]^3} = \int -k\,dt \quad \therefore \quad -\frac{1}{2}[A]^{-2} = -kt + \text{const}$$

$$\therefore \quad [A]^{-2} = 2kt + \text{const} .$$

When $t=0$, $[A]=a_0$ $\therefore$ const $= a_0^{-2}$

$$\therefore \quad [A]^{-2} = 2kt + 1/a_0^2 .$$

When $t = t_{1/2}$, $[A] = a_0/2$

$$\therefore \left(\frac{a_0}{2}\right)^{-2} = 2kt_{1/2} + \frac{1}{a_0^2} \quad \therefore \quad 2kt_{1/2} = \frac{4}{a_0^2} - \frac{1}{a_0^2} = \frac{3}{a_0^2}$$

$$\therefore \quad t_{1/2} = \frac{1}{2k} \cdot \frac{3}{a_0^2} .$$

v is in conc/time, so k is in conc^{-2}/time.

You could use any concentration and time units.

One example is mol^{-2} dm^6 s^{-1}.

see exercises A5, B1, B4 and class examples

(2) *30 points*

Consider the following mechanism proposed for the overall reaction $A + 2B \rightarrow C$:

$A + B \rightarrow X$ rate constant k_1

$B + X \rightarrow C$ rate constant k_2

$X \rightarrow A + B$ rate constant k_3

i) Assuming that the intermediate X is in a steady state, derive the rate law for formation of C.

ii) What are the limiting values of the total reaction order as [B] tends to zero and as [B] tends to infinity?

Show work and justify your answers.

i)
$$0 = \frac{d[X]}{dt} = k_1[A][B] - k_2[B][X] - k_3[X]$$

$$\therefore \quad k_1[A][B] = [X](k_2[B] + k_3)$$

$$\therefore \quad [X] = \frac{k_1[A][B]}{k_2[B] + k_3}$$

$$\frac{d[C]}{dt} = k_2[B][X] = \frac{k_1k_2[A][B]^2}{k_2[B] + k_3}$$

ii)
$$\lim_{[B]\to 0} \frac{d[C]}{dt} = \frac{k_1k_2[A][B]^2}{k_3}$$

second order in B

first order in A

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third order overall

$$\lim_{[B]\to\infty} \frac{d[C]}{dt} = \frac{k_1k_2[A][B]^{\cancel{2}}}{k_2\cancel{[B]}}$$

first order in A and B, so second order overall.

see exercises E1 and class examples

(3) *20 points*

A reaction has k = 30 s^{-1} at 298 K and an activation energy of 50 kJ mol^{-1}. Predict the value of k at 500 K.

$$k = A e^{-\frac{E_a}{RT}} \quad \text{(Arrhenius equation)}$$

$$= A e^{-\frac{50000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol} \times 298 \text{ K}}}$$

$$= A e^{-20.18}$$

$$\therefore A = e^{+20.18} . k = e^{20.18} \times 30 s^{-1} = 1.74 \times 10^{10} s^{-1} .$$

At 500K,
$$k = 1.74 \times 10^{10} s^{-1} \times e^{-\frac{50000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 500 \text{ K}}}$$

$$= 1.74 \times 10^{10} s^{-1} \times e^{-12.03}$$

$$= 1.04 \times 10^{5} s^{-1} .$$

see exercises D1, D2

(4) *20 points*

At 750 K, $\Delta_f G^o$ of atomic iodine is 3 kJ mol^{-1} and the standard state for I_2 is a gas. Calculate the degree of dissociation α of I_2 in a container where 5500 Pa of initially pure I_2 vapor at 750 K comes to equilibrium:

$$I_2\,(g) \rightarrow 2\,I\,(g)$$

Comment: do not assume that α is small compared to 1.

$$\Delta G^{\ominus} = 2\Delta_f G(I) - \Delta_f G(I_2) = 2\times 3\,\mathrm{kJ\,mol^{-1}} - 0 = 6\,\mathrm{kJ\,mol^{-1}}.$$

$$= -RT\ln K \quad \therefore\ K = e^{-\frac{\Delta G^{\ominus}}{RT}} = e^{-\frac{6000\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}mol^{-1}}\times 750\,\mathrm{K}}}$$

$$= e^{-0.962} = 0.382.$$

	$I_2 \longrightarrow$	$2I$
initial activity	$\frac{5500\,\mathrm{Pa}}{10^5\,\mathrm{Pa}} = 0.055$	0
equilibrium activity	$0.055(1-\alpha)$	$2\times 0.055\alpha = 0.11\alpha$

$$K = \frac{(0.11\alpha)^2}{0.055(1-\alpha)} = \frac{0.22\alpha^2}{1-\alpha}$$

$$\therefore K(1-\alpha) = 0.22\alpha^2 \quad \therefore\ \alpha^2 = 4.55K - 4.55K\alpha$$

$$\therefore\ \alpha^2 - 4.55K + 4.55K\alpha = 0$$

now substitute for K:

$$\therefore\ \alpha^2 - 1.736 + 1.736\alpha = 0$$

$$\therefore\ \alpha = \frac{-1.736 \pm \sqrt{1.736^2 + 4\times 1.736}}{2} = \frac{-1.736 \pm 3.156}{2}$$

and α must be positive so $\alpha = \frac{-1.736 + 3.156}{2} = 0.710,$

see exercises 6A.5, 6B.4, class examples and the last test.